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RAMAN MICROPROBE ANALYSIS OF STUCCO SAMPLES FROM THE BUILDINGS OF MAYA CLASSIC COPAN

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ABSTRACT

Micro-Raman spectroscopy has been applied to painted stucco samples from three buildings at the Maya site of Copan, Honduras. The buildings, Clavel (AD 450-550), Ani (AD550-650) and Temple 22 (AD730,) date from three phases of the Classic Period (AD400-820) acropolis construction. The red pigment has been identified as hematite and the stucco as a mixture of calcite particles dispersed throughout a calcite based lime wash stucco. The physical structure of the stucco changed through time indicating a refining of production techniques over this period. By combining Micro-Raman

spectroscopy with other micro-ATR infrared spectroscopy and environmental scanning electron microscopy a detailed investigation of the materials and production techniques used to decorate these buildings has been made. Differences in the mineralogy of the red pigment used on each building indicate a different geological pigment source for each period.

INTRODUCTION

The Maya city of Copan in Honduras has been the subject of archaeological investigation for over 100 years [1,2,20,21,24,27]. Research into its Classic period monumental architecture and its underpinning socio-political development has documented not only the externally visible structures but, as a result of tunneling beneath the Acropolis, a detailed architectural history dating back to the Early Classic period. [10,11,31,19,23]. Erosion of the eastern side of the Acropolis by the Copan River has exposed a huge vertical section, or 'corte', through which the construction history may be viewed in profile. Over 4 km of interlinking tunnels into this section have exposed some 20 buried buildings, thus permitting the comparison of building styles as well as functions [21]. The burial of these structures involved the partial demolition of their upper parts and infilling of lower rooms before they were covered with mud and rock prior to the construction of new buildings [23]. In some cases up to eight buildings were overlain in this manner.

The lowest levels of the Acropolis exhibit earthen structures coated with a mixture of red pigment and clay that date to the founding of the Copan Classic Dynasty in AD 426, after which time architectural style changed dramatically and the focus of construction in the valley moved to the present Acropolis site. Early architecture included earthen structures and stone masonry buildings decorated with stucco and painted murals. While the next 400 years saw change in both architectural style and decoration, all the buildings shared one common feature; their masonry walls were coated with lime stucco and painted. Beyond this basic coating there are numerous differences in decorative style including polychrome murals in red, yellow and green pigments, stucco moulded relief and, later, painted relief carvings.

The exposure of so many buildings beneath the Acropolis provides a singular opportunity not only to compare architectural style and building function through time but to also examine quite specific and detailed aspects of their construction. One such aspect that has received little investigation to date is the physical and chemical make-up of the stuccos and pigments used in the decoration of these buildings. This paper concerns a project aimed at identifying the materials used as pigments, investigating the materials used and the processes involved in preparing the stucco as well as in ascertaining temporal and spatial variability. It reports on the results of an analysis of samples from buildings representing the Early, Middle and Late Classic Periods of construction at Copan.

Micro-Raman spectroscopy has been used extensively over the last decade to examine archaeological and art samples [4,8]. While it has been used to identify pigments on rock art [6,17], frescos [3,7,9] and painted pottery [26], little work has been focused on Maya stucco and pigments. Some early petrographic and X-ray diffraction analysis determined the composition of the stucco and mortar for different Maya sites [14,15,16]. Early pigment studies focused on the composition of the distinctive pigment *Maya Blue* a stable combination of indigo and palygoskite clay [18]. More recently a Raman spectroscopy investigation of pigments at the Maya site of Ek'Balam identified a range of pigments, including hematite, goethite, calcite, cinnabar and *Maya Blue*[25].

Micro-Raman spectroscopy is particularly applicable to archaeological samples as it is non-destructive, has a high spatial resolution and is especially useful for the detection of mineral samples where the characteristic bands are mainly below 700 cm^{-1}. Thus, as individual particles can be analysed it is easier to identify mixtures and isolate minor contaminants in samples. By employing Micro- Raman spectroscopy in combination with other non-destructive techniques such as micro-ATR infrared spectroscopy and environmental scanning electron microscopy (ESEM) combined with micro-X-ray analysis, we hope to provide a comprehensive study of the mineralogy and composition of these samples, the results of which should provide an insight into the questions considered by this study and, eventually, broader issues concerning sociopolitical change in this Maya polity .

EXPERIMENTAL

Samples

The painted stucco samples came from separate Classic period buildings. The earliest sample is from the Clavel building (Figure1a), a masonry structure covered with stucco and paint from the Early Classic period (AD 450-550). Clavel is situated on the western side an early group of structures around an early court including the structure Yenhal . These early structures lie beneath what is now the East court. It was covered by rubble fill before multiple building levels above it were constructed over 300 years to form the base of what is now Structure 10L-16 [19].

A second sample was obtained from the Ani building (Figure1b) which is the superstructure of the 'Ante' platform located below the eastern side of the East Court [21]. This masonry building of Middle Classic age (AD541-542) has stucco and paint on its walls with and modeled decoration on the 'Ante' platform. It was also covered by fill and overlain by Late Classic buildings.

The third sample came from the partially reconstructed Late Classic (AD 730) structure, Temple 22 (Figure 1c). As it was part of the last phase of construction at Copan it was exposed to the elements, and after the site was abandoned it became overgrown by jungle and many of its walls collapsed. Situated at the north side of the Final East Court, this temple has carved masks on each corner that still retain residues of stucco and paint layers in the deeper recesses of the masks. The best sample locality at Temple 22 was the southeast corner.

All samples taken were exfoliating from the wall surfaces and they had no adhering particles of the substrate. Four or five fragments were available from each sample location. Single fragments of each sample were set in Araldite M resin and the cross-sections were polished using diamond paste prior to analysis by ESEM and micro-ATR infrared spectroscopy. Standard reference materials of several minerals including specular and earthy hematite, goethite, magnetite and pyrolusite were obtained from Wards Scientific.

Raman spectroscopy

Spectra were recorded directly on the pigment and stucco surfaces using a Renishaw Model 1000 microRaman spectrometer consisting of an Olympus BH2-UHA microscope with a 50x objective attached to a spectrograph equipped with an electrically cooled Charged Coupled Detector (CCD). Excitation was from either a strongly polarised Spectra-Physics Model 127 He/Ne laser operating at 632.8 nm or a diode laser emitting at 785 nm. The laser power for both lasers was reduced using an optical filter to approximately 0.7 mW at the sample. The lower laser powers were used to avoid inducing thermal changes to the mineralogy of the iron oxide minerals. Integration time was around 50 s per accumulation and up to 5 accumulations were co-added to produce the final spectrum.

FT-Raman micro-spectra

FT-Raman micro-spectra were recorded using a Bruker IFS66 instrument with a FRA 106 Raman module attachment. A Nd^{3+}/YAG laser with a nominal maximum power of 700 mW at 1064 nm was utilised in microscopic mode with a circular footprint of 100 µm. Spectra were recorded at 4 cm^{-1} spectral resolution and 2000 scans co-accumulated over the wavenumber range 100 – 3200 cm^{-1}; the accumulation time for each spectral sampling point was 1 hour. Several replicates were studied for each species.

Micro-attenuated total reflectance infrared spectra

Spectra were recorded by contacting the ATR crystal directly onto the polished surfaces of the mounted cross sections. Individual selected areas of the samples could thus be measured. The spectrometer was a Nicolet Nexus 870 FTIR with a Continuμm Infrared microscope equipped with an ATR objective incorporating a Si internal reflection element (Thermo Electron Corp., Madison, WI). The system is equipped with a liquid nitrogen cooled MCT detector. Spectra were recorded with a resolution of 4 cm^{-1} within a spectral range of 4000 - 700 cm^{-1} for 128 co-added scans. Spectra were manipulated using GRAMS/32 software package (Galactic Corp. Salem, NH)

ESEM and micro X-ray analysis

Analysis was carried out on a FEI Quanta 200 scanning electron microscope (SEM). Environmental mode was used and the samples did not require coating prior to analysis. Elemental analysis was carried out using an EDAX microanalyser with a 20 kV accelerating voltage and pressure of 2.0 Torr. Analysis was carried out on the cross-sections set in resin.

RESULTS AND DISCUSSION

Visual Microscopy

The samples were initially surveyed using a visual microscope with 10x and 20x objectives. The stucco in each sample consists of a coarse under layer made up of a fine uniform matrix material interspersed with coarse white and grey angular particles. This layer varies in thickness between the samples. Covering this is a fine stucco layer consisting of a very fine homogenous matrix with fine grained angular particles dispersed throughout. Covering the stucco is a layer of pigment which varies in thickness between the samples. The structure suggests a practice of smoothing the coarse undulations of the basal wall material with coarse stucco and then creating a smooth painting surface with a finer more highly ground material. This is a similar practice to that employed by the Romans and later Europeans [5,7,9].

The stucco layers of the three samples vary in their thickness, Table 1. The thickness of both the coarse and fine layers decreases and the particle size range reduces from the Early to Late Classic period samples. The Clavel building has flat walls with some recessed walls and block edges with very little relief shaping. It is covered with a single stucco/paint assembly. The stucco layer is up to 4 mm in thickness and exhibits a large particle size range (up to 200 μm in length in some cases). The particles are angular and roughly shaped; there are no smooth spherical shapes. The fine stucco layer, up to 200 μm thick, is also filled with angular particles but these are more consistent in shape and size, probably as a result of more thorough grinding during preparation of the applied material. A single thin paint layer covers the stucco. The particles in the paint layer are finer and more consistent in size. The surface of the paint layer has patches of yellow, cream and dark brown material adhering to it. This single layer covers all the walls that have been exposed to date.

The Ani building has flat walls with a red covering, some of which has evidence of a second paint coating. Some wall sections have multi-coloured relief patterns and murals. Most sample fragments from this building exhibit two stucco/paint layers. They have a thicker stucco layer covered by a fine stucco layer but these layers are much thinner than those observed in the earlier Clavel sample, Table 1. The lower coarse stucco layer shows a broad particle size range but the subsequent layers have a narrower size range consistent with more grinding. The first paint layer is the thickest, consisting of a finely ground pigment with few particulate inclusions. The second stucco/paint assembly has a coarse covering layer followed again by a finer ground stucco layer prior to the paint layer. The thin upper paint layer was probably eroded by weathering prior to the building's burial. The upper surfaces of the fragments are covered with patches of white and yellow-brown particles and crystals. The patches of red pigment on the white surfaces of the fragments are the remains of paint from another paint layer.

Temple 22 yielded at least 15 and possibly up to 20 layers of paint/stucco in some recesses of the carved mask on the south east corner. The coarse stucco layer on each fragment is of similar thickness with a broad range of particle sizes. The finer upper layer is consistent with the previous samples with fine angular particles. The number of stucco/paint layers on this building is significantly greater than the one or two layers found on the earlier ones. The same process has been maintained when reapplying each stucco layer. Some fragments differ in that the paint layer is covered by a highly crystalline coating of calcite. This layer contains no fragments or particulates mixed into the calcite matrix. The paint residues on the temple also show evidence of organic attack from algae or similar.

The grey and white particles throughout all samples are angular, crushed material. Lime stucco requires the addition of particulate material to reduce shrinkage and cracking when drying. This material can be crushed limestone, quartz sand, and in some instances volcanic ash has also been used [15]. The angular crushed particles present in these samples are not consistent with the use of water-rounded rock or sand as the filler. All samples contain small black and red particles dispersed throughout the white/grey matrix. The black particles are mostly elongated and vary in size from 10 to 30 μm length, while the red particles are smaller (10-20 μm) and angular.

Raman spectroscopy

The spectra in Figure 2 represent standard samples of some of the most common red and brown pigment minerals. These can be differentiated by the band positions of each mineral. Hematite can be distinguished by the major bands at 610, 410 and 298 cm^{-1}, goethite by the major bands at 398 and 555 cm^{-1} and magnetite by a broad band at 660 cm^{-1}. Manganese dioxide as pyrolusite is distinguished using the large broad bands at 580 and 655 cm^{-1}. The published spectra for pyrolusite vary between authors and can be problematic because of the large number of manganese oxides/hydroxides which undergo thermal transformations at high laser powers. Low laser powers were used in this instance but confirmation of the presence or absence of Mn by ESEM-EDX was used to verify the spectral interpretation [3,22,28]. Figure 3 represents common minerals found in lime stucco. Calcite is the main component of lime based stucco and has distinctive Raman bands at 1087, 712 and 284 cm^{-1}. Quartz is often used as a fill material and has a band at 464 cm^{-1}. Other materials were matched to published spectra [3-9].

Stucco Layers

The samples were first investigated as received, with no pretreatment undertaken prior to analysis. Spectra were recorded of the upper painted layer, the reverse, stucco side of the samples, which could have been attached to the substrate rock surface, and the side surfaces on each sample. The surfaces were visually surveyed to identify any inclusions as well as the main matrix material of both the paint material and the substrate stucco. Spectra were recorded on a significant number of particles as well as on the fine matrix material. The stucco matrix always gave the spectrum of calcite, which is consistent with the use of lime wash stucco. Both the white and grey angular particles and the fine matrix material gave spectra with bands at 1085, 712 and 283 cm^{-1}, indicative of calcium carbonate, calcite polymorph. FT-Raman spectra of the stucco matrix contained a broad feature at about 770 cm^{-1} assigned to hydrated calcium oxide/hydroxide [9]. The reaction of slaked lime with carbon dioxide from the atmosphere forms calcium carbonate in the stucco. The presence of calcium oxide/hydroxide in the sample indicates that this reaction was incomplete when the stucco dried out. Similar results have been found by one of us for Roman and Norman stucco [9].

There was no evidence of quartz or other mineral inclusions in the stucco. The underside of the stucco was examined for evidence of the underlying wall material but none was found. This is not unexpected with exfoliated samples where adhesion to the surface is poor anyway. The small black particles in the matrix all gave spectra with the broad bands at 1500 and 1350 cm^{-1} indicative of carbon. The broadness of these bands indicates an amorphous carbon with low crystallinity. Charcoal residues from the lime burning process are the most likely source of these particles. Limestone was burnt in a kiln to produce lime, the starting material for the production of lime stucco. One lime kiln has been found in the Copan valley dated to AD750 - 900 [1] confirming that this technology was in use by the Late Classic period. The only other visible constituent is very small red particles, the spectra of which show the seven distinct bands of hematite.

Clavel Building

The earliest building, Clavel, has a single painted layer with no evidence of repainting. The red pigments on the eight fragments available from this building all contain the iron oxide, hematite. The spectra recorded on all fragments are identical for both the fine matrix and some red particles. Small dark red glassy particles in the matrix were identified as quartz by a band at 464 cm^{-1}. The rounded nature of these particles suggests that they may be due to quartz grains incorporated into the pigment during the grinding processes. Scattered throughout the pigment layer are small flaky particles with a metallic sheen (Figure 5a). The Raman spectra of these particles have three bands at 611, 450 and 237 cm^{-1} which are characteristic of the titanium dioxide phase rutile, Figure 4. Although rutile can be a contaminant in natural iron oxide deposits, the range of large and small individual particles of rutile in the paint suggests that the rutile was added to the iron oxide pigment rather than being part of the original ore deposit. This addition could have been made to enhance the colour or properties of the paint. Micro-ATR infrared spectra of the painted layer of the cross sectioned sample confirm the presence of quartz with bands at 798 and 780 cm^{-1}, and calcite. Bands at 3697, 3668, 3653 and 3620 cm^{-1} indicative of OH stretching vibrations along with the OH bending vibrations at 935 and 915 cm^{-1} suggest that the clay present is kaolinite. Spectra of the stucco layers have bands only of calcite, with no clay or quartz.

The ESEM image of the sample, Figure 5a, shows the particulate nature of the paint layer and the sharp delineation between the paint and stucco layer. ESEM-EDX analysis of the cross section confirms the data obtained by Raman spectroscopy and micro-ATR infrared analysis. High levels of Al and Si are found throughout the red pigment layer confirming the presence of alumino-silicates in the matrix. Some particles in the paint layer are almost pure SiO_2 confirming quartz particles. Particles with high levels of Ti were also identified throughout the red layer as well as in a large area of pigment contamination in the middle of the coarse stucco layer. The rutile can be confirmed as part of the pigment and not contamination from the burial material. The particles are found as localized contaminants and are not spread through out the pigment as would be expected if the material were part of the burial material. Particles on the surface of the sample contained phosphorus and result from organic contamination of the surface by algal growths since the tunnels were open to the environment. The stucco layer consisted of calcium, carbon and oxygen consistent with calcite mineralisation.

Ani Building

The samples from this Middle Classic building contain more than one layer of paint and thus agree with visual observation of wall surfaces exposed during tunneling. The Raman spectra of the red pigment of each layer and fragments were consistent. Each has the distinctive bands of hematite and a very weak band around 660 cm^{-1}. A number of dark glassy particles in the red matrix were identified by the presence of the 464 cm^{-1} band of quartz. FTIR-ATR spectra were recorded on the painted layer of the sample cross section. Hydroxyl stretching bands at 3695, 3618, and 915 cm^{-1} suggest the presence of clay although there are insufficient bands to confirm the type of clay. Bands at 798 and 780 cm^{-1} confirm the presence of quartz in the pigment. The stucco layers and particles gave Raman bands at 1086, 712 and 285 cm^{-1} consistent with the calcium carbonate make-up of the matrix. The contaminating red and black particles were identified by Raman spectroscopy as hematite and carbon, respectively.

The ESEM image, Figure 5b, shows the two distinct paint layers in this sample. ESEM-EDX analysis of the two paint layers confirms a similar elemental composition in the two paint layers. Each paint layer was high in Fe with minor amounts of Al and Si found throughout. These latter two elements are consistent with the presence of clay in the pigment. Both stucco layers have high calcium levels throughout with carbon and oxygen and only small amounts of iron-containing particles.

Temple 22

The samples from the Late Classic Temple 22 are multiple flakes from different layers of paint and stucco. The red pigment on these fragments is much brighter and lighter than that on the other two samples. The paint on all fragments gives consistent hematite spectra with the seven bands plus an intense band at 660 cm^{-1} indicative of magnetite which has a distinctive feature at this position, Figure 6. This intense band is of similar intensity as the 610 cm^{-1} band of hematite. Individual magnetite particles were not detected in the paint matrix, suggesting that the magnetite is an impurity in the hematite material rather than an admixture to the pigment. This impurity could indicate that a different source material of hematite has been used to paint this Temple. Rounded particles of glassy quartz were identified in the paint matrix by the band at 464 cm^{-1}. In many areas the red paint layer is covered by a white calcite layer and on the top of this layer are small patches of red pigment. These were also identified as the same hematite as the main layer. These red patches are probably parts of the covering paint layer still adhering to the stucco. FT-Raman analysis of the stucco also reveals the presence of the broad feature at 770 cm^{-1} of calcium oxide/hydroxide. There are small CH bands at 2872 and 2950 cm^{-1} indicating an organic component in the surface material. A weak feature at 3200 cm^{-1} could indicate –NH modes. Visual observation of the sampling site at the Temple showed a great deal of black discolouration on the surface layers of stucco/paint residues suggesting there has been algal colonisation in the past. Algal growth has been reported on the temples at Tikal [12], another Maya site in this tropical region.

FTIR-ATR spectra recorded on the sample cross section confirmed the presence of quartz in the painted layers but no OH stretching bands were observed suggesting there are no clay minerals in the material used for this pigment. The stucco layers gave clear calcite spectra with no other bands observed. ESEM image Figure 5c, of the sample cross section shows clear coarse and fine stucco underlayers with angular particles of calcite dispersed throughout. ESEM-EDX analysis confirms the stucco layers are high in Ca with C and O. ESEM-EDX confirms that the paint layer in this instance is high in Fe with some Si but little or no Al. The paint layer is covered by a more crystalline calcite layer. This layer is interspersed with voids and occasional bands of more solid material but contains no particulate material, Figure 5c. The covering layer is almost pure calcium with low carbon and oxygen. The bands in this covering are very high in Si content with small amounts of calcium, carbon and oxygen. This covering composition suggests the re-crystallisation of calcite formed from the leaching of un-reacted calcium hydroxide in the stucco interspersed with bands of almost pure silicate. Large amounts of stucco and paint have been washed from the surface of the temple through the action of the intense wet season rains that occur in this region.

Major mineralogical differences have been identified in these three samples. The earliest sample from the Clavel building contains particles of rutile in the red pigment matrix. Rutile is not found in any other sample. The red hematite pigment also contains small amounts of clay, most likely kaolinite, which is most likely part of the original mineral composition. The Ani building samples also have clay present in the red hematite pigment. The Temple 22 sample does not have clay in the hematite pigment and shows a magnetite band at 660 cm^{-1} in the Raman spectra which is not present in the other two samples. These differences are enough to be able to differentiate between the minerals used and could finally be used as a geographical mineralogical sourcing of the building materials.

CONCLUSIONS

The use of Raman micro-spectroscopy has enabled the identification of the minerals used in the preparation of pigments applied on these three Maya buildings at Copan. The identification of contaminants in the materials has enabled us to differentiate between the materials used on each building and the variation suggests a change in the source material used over the 400 hundred years represented by these buildings. Although the thickness of stucco used has decreased over time, the mineral composition of the material has not changed. The fill material used is consistently limestone with minor contaminants present from the processing of the limestone to form lime. This finding is similar to those from other Maya sites where limestone is the only fill used [15]. The combination of analytical techniques in this study has provided a more thorough understanding of sample composition, enabling enhanced differentiation between the samples. Samples from other buildings at the site are currently being studied to extend this investigation to answer questions regarding change through time that may correspond to changing socio-political organization in this Maya polity.

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Figure Captions

Figure 1 Stucco and paint fragments a) Clavel building with single paint layer, b) Ani building with two paint layers c) Temple 22 with crystalline coating over paint layer.

Figure 2 Raman spectra of standard oxide minerals from top hematite, magnetite, goethite and the manganese oxide, pyrolusite. (785 nm laser, 0.7 mW, 5 scans of 50 s)

Figure 3 Raman spectra of calcite (top) and quartz (633 nm laser, 0.3 mW, 5 scans of 50 s)

Figure 4 Raman spectra of rutile particles in red pigment Clavel building. (785 nm laser, 5 scans of 50 s)

Figure 5 SEM micrographs of a) Clavel sample, b) Ani sample, c) Temple 22. Paint layers are indicated by arrows.

Figure 6 Raman spectra of red pigment from the three samples showing characteristic bands for hematite. Note the more intense band at 660 cm^{-1} for the Temple 22 sample. (633 nm laser, 5 scans of 50 s)

Table 1

Sample	Coarse Stucco Layer		Fine Stucco Layer		Paint Layer
	Thickness (mm)	Particle size (μm)*	Thickness (μm)	Particle size (μm)*	Thickness (μm)
Tunnel 28, Clavel Building	2-4	50 - 200	100 - 200	10 – 58	10 -20
Ani(Layer 1) Building(Layer 2)	1.1 0.5	20 – 300 10 - 30	100 – 130 100-110	10 -30 10 – 30	60 25
Temple 22	0.7	20 - 300	100 - 130	10 – 30	100

*Longest dimension

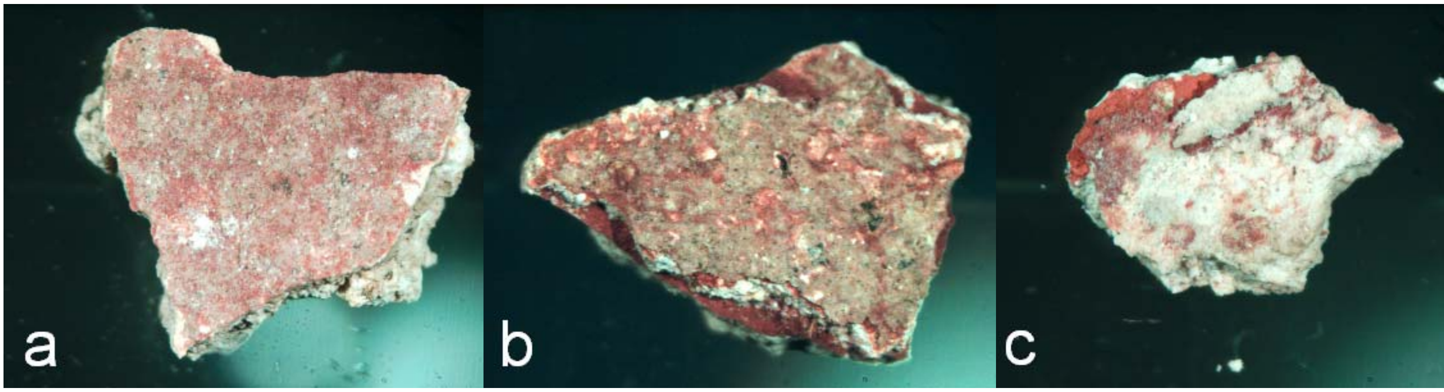

Figure 1

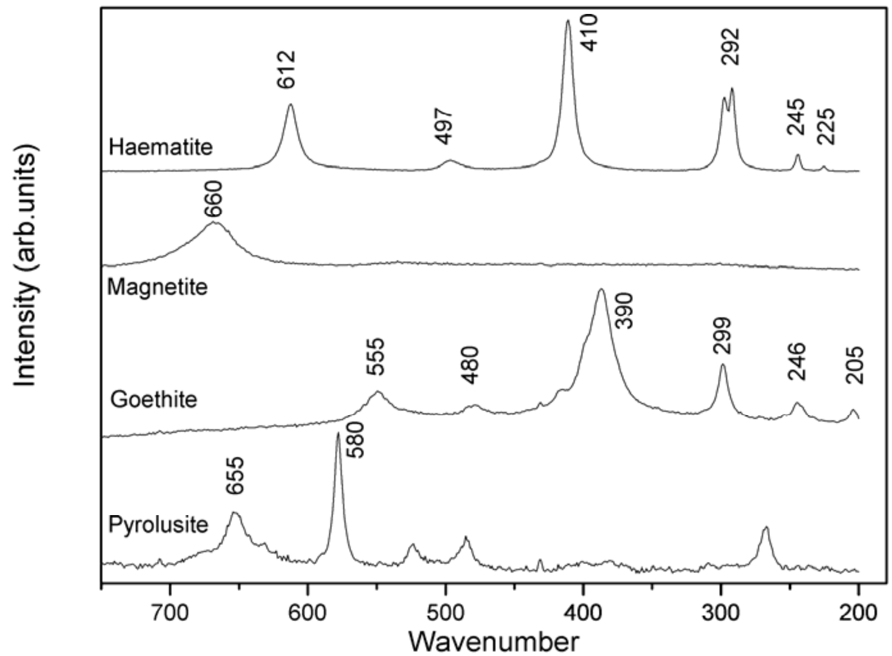

Figure 2

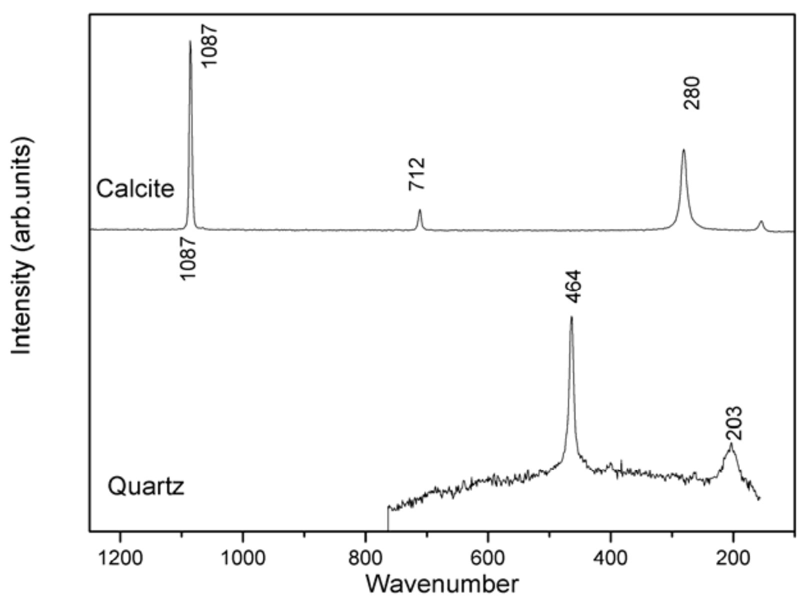

Figure 3

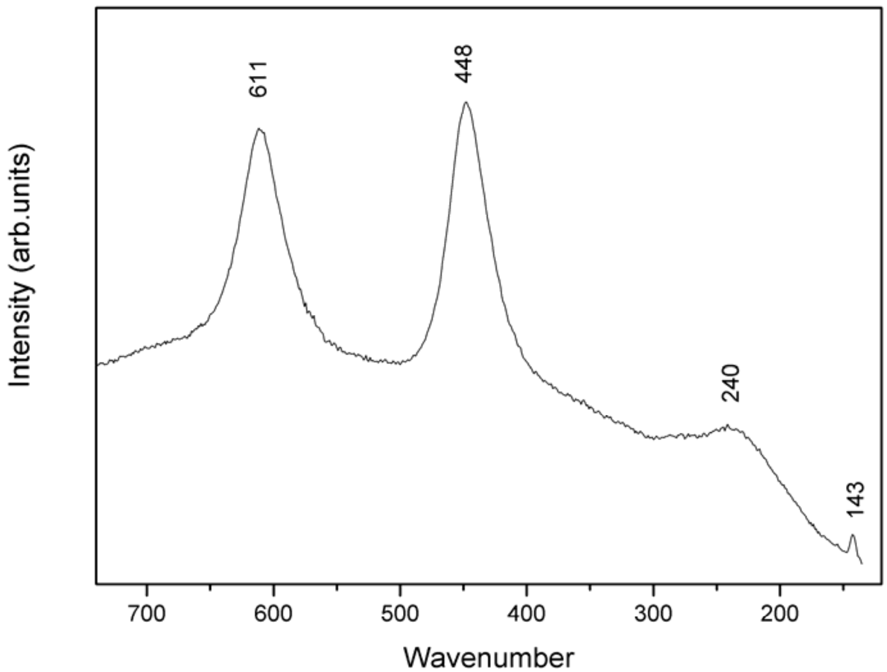

Figure 4

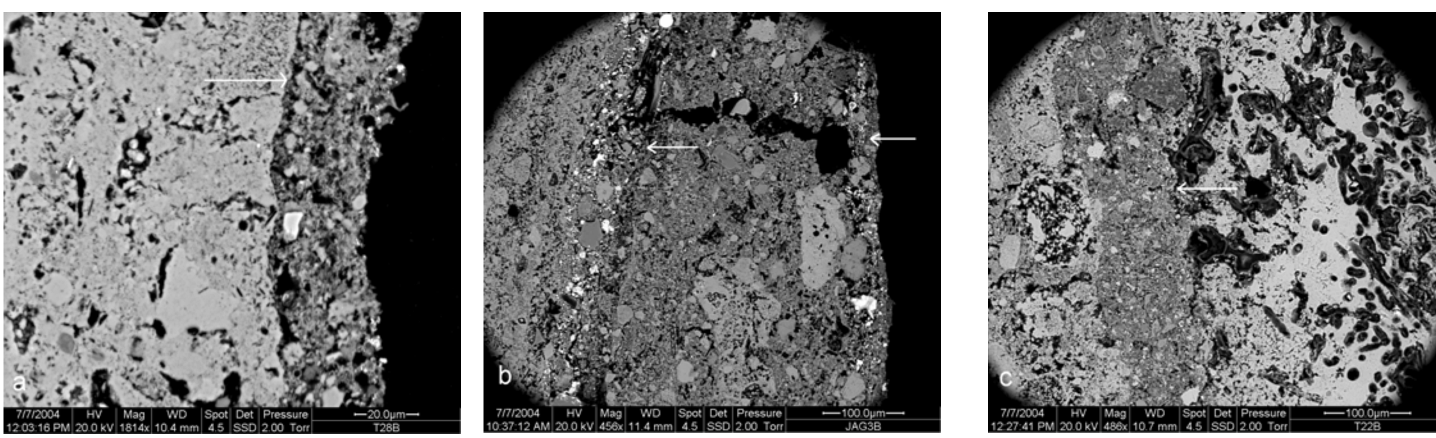

Figure 5

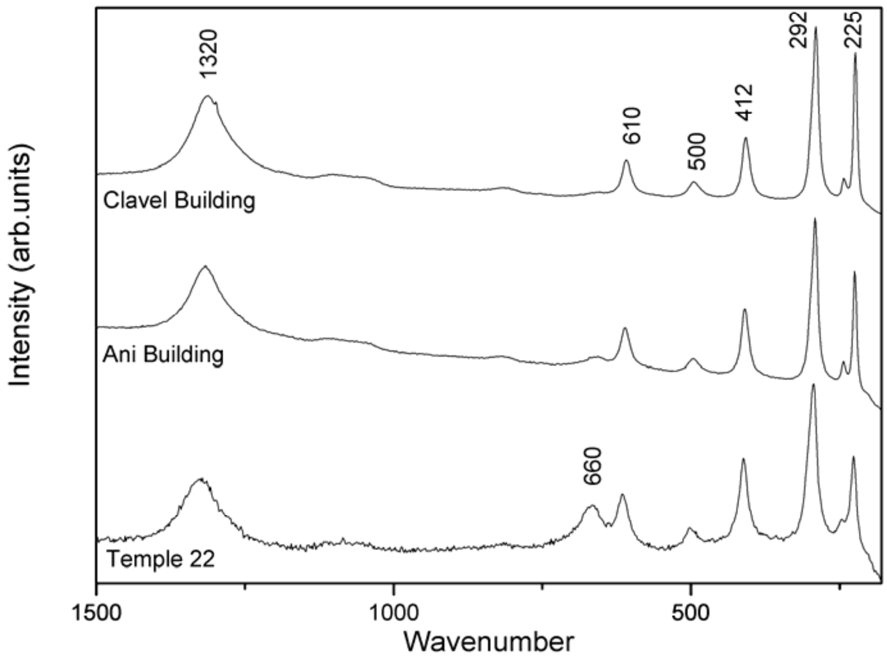
1320
610
500
412
292
225
660
Clavel Building
Ani Building
Temple 22
Intensity (arb.units)
1500
1000
500
Wavenumber

Figure 6